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## (54) PRODUCTION OF VEGETABLE SQUALANE CONCENTRATE

(57)Abstract:

PROBLEM TO BE SOLVED: To efficiently produce a vegetable squalane concentrate derived from a plant in a relatively short time according to extremely simple operations by treating a raw material such as a vegetable oil and fat with urea or thiourea in an organic solvent.

SOLUTION: A mixture, obtained by mixing (A) a vegetable oil and fat containing squalene or (B) a deacidified and deodorized distillate thereof with (C) an organic solvent and (D) urea or thiourea and having  $\leq 8$ wt.% moisture content is heated at 40-120°C and then cooled to 0-35°C. The components (D) and (C) are subsequently removed and the obtained product is hydrogenated to provide the objective concentrate having  $\geq 85\%$  squalane purity and fluidity without clouding even at -40°C. Furthermore, the component (A) is preferably at least one selected from the group consisting of olive oil, corn oil, soybean oil, safflower oil, rice bran oil, wheat germ oil, palm oil and sesame oil and the component (C) is preferably an alcoholic solvent (e.g. isopropyl alcohol).

## CLAIMS

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### [Claim(s)]

[Claim 1] The water garnish of the vegetable fat and oil containing squalene, or its deoxidation deodorization distillate After heating the mixture of 8 or less % of the weight of moisture content which mixed with an organic solvent, a urea, or thiourea, and was obtained at 40-120 degrees C and cooling at 0-35 degrees C after that, the crystal and said organic solvent of a urea or thiourea are removed. The manufacture approach of the vegetable squalene concentrate characterized by for squalene purity being 85% or more, and for at least -40 degrees C not becoming cloudy, but obtaining a fluid \*\*\*\* concentrate.

[Claim 2] The approach of claim 1 which is chosen from the group which vegetable fat and oil becomes from olive oil, corn oil, soybean oil, safflower oil, rice bran oil, a wheat germ oil, palm oil, and sesame oil and which is a kind at least.

[Claim 3] Claim 1 chosen from the group which an organic solvent becomes from alcoholic solvent, a glycol system solvent, and a hydrocarbon system solvent, or the 2 approaches.

[Claim 4] The approach of of claim 1 - 3 any 1 terms that the iodine number of the above-mentioned water garnish is one or less.

[Claim 5] The mixture of 8 or less % of the weight of moisture content which was mixed with an organic solvent, a urea, or thiourea, and obtained the vegetable fat and oil containing squalene, or its deoxidation deodorization distillate After heating at 40-120 degrees C and cooling at 0-35 degrees C after that, the crystal and said organic solvent of a urea or thiourea are removed. The manufacture approach of the vegetable squalene concentrate which carries out hydrogenation of the obtained product and is characterized by for squalene purity being 85% or more, and for at least -40 degrees C not becoming cloudy, but obtaining a fluid \*\*\*\* concentrate.

[Claim 6] The approach of claim 5 which is chosen from the group which vegetable fat and oil becomes from olive oil, corn oil, soybean oil, safflower oil, rice bran oil, a wheat germ oil, palm oil, and sesame oil and which is a kind at least.

[Claim 7] Claim 5 chosen from the group which an organic solvent becomes from alcoholic solvent, a glycol system solvent, and a hydrocarbon system solvent, or the 6 approaches.

## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to concentration of useful vegetable squalane in fields, such as perfumery and cosmetics and drugs.

[0002]

[Description of the Prior Art] The hydrocarbon used as a raw material for perfumery and cosmetics and drugs is classified into the hydrocarbon represented by the liquid paraffin which is the hydrocarbon of the petroleum origin, and the hydrocarbon represented by the squalane which is the living thing origin. Squalane is colorlessness, no odor, and the tasteless oily liquid of low volatility, and is set to one at the oil phase raw material of the perfumery and cosmetics which had a lighter oily feel compared with the liquid paraffin, were excellent in the permeability and lubricity to the skin, and were most excellent since elongation was good and it was very easy to emulsify it, and drugs.

[0003] conventionally, the used natural squalane is represented by AIZAME -- mainly -- deep sea -- a \*\* -- it is animal squalane which uses a shark as a start raw material. It is what carried out hydrogenation of the squalene isolated preparatively out of liver oil, such as AIZAME, and this animal squalane excels [congealing point] in -55 degrees C or less and freeze thaw stability, and its safety is also high.

[0004] however, the deep sea which recent years come and is the raw material of natural squalane uniquely substantially -- a \*\* -- in the Philippines and Indonesia which are the principal production area of a shark, India, Sri Lanka, Africa West Coast, and the Caribbean Sea, a fish catch falls by change of climate, overhunting, etc., and the amount of supply does not catch up with the amount of need, but the inclination of a shortage of money continues. Moreover, a rise of the latest animal protection movement accelerating the inclination of a shortage of money further further is being able to predict enough.

Furthermore, the inclination to evade the natural resource of the animal origin is also strong every year.

[0005]

[Problem(s) to be Solved by the Invention] Then, this invention persons paid their attention to the squalene of the vegetable origin as a raw material of natural squalane. Although it was known for many years that squalene is contained in vegetation especially fruits, and a seed, there are very few the contents, it is very difficult to extract, separate and condense squalene industrially, and it has been thought that industrialization is impossible. For example, as for the squalene content, the olive oil said to be contained comparatively so much is also 0.2 - 0.7 % of the weight.

[0006] By the way, although edible oil including olive oil performs deoxidation deodorization at that purification process, squalene is obtained as a distillate at this time together with various unsaponifiable matters other than free fatty acid or squalene. Since this distillate is surely generated when manufacturing edible oil, if squalene can extract, dissociate and condense effectively from this distillate, it is stabilized and can supply the squalane of the vegetable origin.

[0007] However, as for the presentation of the unsaponifiable matter contained in the deoxidation deodorization distillate of edible oil including olive oil, many components which it is various and squalene and physical properties resemble, such as hydrocarbons, sterols, methyl sterols, triterpenes, and a tocopherol, are also contained. Therefore, it has been made very difficult to condense squalene to high concentration.

[0008]

[Means for Solving the Problem] This invention etc. found out a urea or that thiourea processing was carried out or vegetable squalane could be efficiently condensed for said vegetable fat and oil or its deoxidation deodorization distillate in an organic solvent a urea or by carrying out thiourea processing and carrying out hydrogenation after that in the organic solvent for the water garnish of the vegetable fat and oil containing squalene, or its deoxidation deodorization distillate.

[0009] Although olive oil, corn oil, soybean oil, safflower oil, rice bran oil, a wheat germ oil, palm oil, etc. are those deoxidation deodorization distillates, the raw material which can be used for this invention is olive oil, corn oil, or rice bran oil preferably, and is the deoxidation deodorization distillate

of olive oil, corn oil, or rice bran oil still more preferably. These raw materials do not necessarily need to be single classes, and may mix two or more kinds.

[0010] Although a vegetable squalane concentrate is mainly manufactured in an organic solvent in this invention by the urea or the method of carrying out thiourea processing and removing an impurity after carrying out hydrogenation of the A raw material like the above-mentioned, a vegetable squalane concentrate can also be manufactured by the approach of carrying out hydrogenation of the B raw material as it is, a urea or after carrying out thiourea processing, removing an impurity and condensing squalene. Also in which approach, a urea or thiourea processing is good to carry out by the approach of heating the mixture of 8 or less (it is desirable it being especially 5 or less % of the weight 6 or less % of the weight) % of the weight of moisture content which mixed an organic solvent, a urea, or thiourea and obtained the raw material (or water garnish of a raw material) at 40-120 degrees C, and cooling at 0-35 degrees C after that. removing the crystal and said organic solvent of a urea or thiourea after cooling -- A -- law -- direct and B -- in law, by carrying out hydrogenation of the obtained product (squalene concentrate) according to a conventional method, squalane purity is 85% or more, at least -40 degrees C do not become cloudy, but a fluid \*\*\*\* squalane concentrate can be obtained.

[0011] In addition, hydrogenation can use the well-known approach of performing to the bottom of ordinary pressure or pressurization using a nickel catalyst etc. this invention -- like the above-mentioned -- A -- law and B -- although any of law may be applied -- A -- the squalane of a high grade can be obtained very efficiently by carrying out hydrogenation of the raw material and making it into the one or less iodine number by law, before carrying out [ a urea or ] thiourea processing. However, since a urea or the decline in the yield of squalane which hydrogenation must be again performed if thiourea processing is carried out, and is the purpose of this invention is caused and a process is complicated while the iodine number had exceeded 1, it cannot be said to be an advantageous approach. In addition, deoxidation processing may be carried out and additional processing of carrying out rectification processing between hydrogenation, a urea, or thiourea processing in advance of hydrogenation etc. may be carried out.

[0012] Without performing - hydrogenation B law on the other hand, a urea or approach - which carries out thiourea processing The inclusion fractionation effect by the urea or thiourea of the straight chain unsaturated hydrocarbon (squalene and a carbon number are comparable) and squalene which are the main constituent of an impurity Since it is smaller than that of squalane, normal paraffinic hydrocarbon with a comparable carbon number, and squalane, since a lot of ureas or thiourea is needed for removal of this impurity (straight chain unsaturated hydrocarbon) and the yield of squalene falls to coincidence -- A -- effectiveness is somewhat inferior to law.

[0013] In this invention, although each of a halogenated hydrocarbon system, a ketone system, hydrocarbon systems, alcoholic systems, ester systems, etc. can use it and the mixture may be used as an organic solvent, use of n-alkane, n-alkene, straight chain saturated fatty acid system ester, etc. has trouble in processing, and is not desirable. Desirable things are a ketone system, an alcoholic system, and a hydrocarbon system solvent, and are alcoholic solvent, especially C1 - C4. Use is desirable. If abundant [ if the amount of these solvents used is little, the yield of the specified substance not only falling but workability is not good, and ], the loss of a solvent will be large and will lead to a facility or increase of a manufacturing cost. Generally, 0.2 to 100 times as many use as this is appropriate to the weight of a raw material, and the use which is about 0.3 to 10 times is especially desirable.

[0014] Furthermore, as a urea or thiourea, the industrial use urea and industrial use thiourea which conform to commercial JIS can be used. Although decided with the amount of the impurity contained in a raw material, if the amount of a urea and the thiourea used is little, removal of an impurity is not fully performed but it must repeat processing again. If abundant, inclusion not only of an impurity but the specified substance slack squalane will be carried out to coincidence, and it will cause decline in yield. As for especially the amount used, it is desirable that they are about 0.3 to 5 times 0.2 to 20 times to raw material weight.

[0015] Although this urea or thiourea processing should just be carried out by serial simultaneous in a raw material, an organic solvent, a urea, or thiourea by teaching a reaction machine (container which can

be sealed [ product / made from glass lining / the product made from stainless steel which has an agitator or a shaker, and can heat cool, and has a capacitor or ]), it is desirable to usually add a urea or thiourea in the solution which made the organic solvent dissolve or distribute a raw material. However, the sequence of preparation does not influence a treatment effect.

[0016] while preparing the raw material, the organic solvent and the urea, or thiourea of the specified quantity and stirring or shaking -- ordinary temperature -- or 40-120 degrees C is preferably mixed enough at 50-80 degrees C. After checking that it has been mixed enough, it cools slowly. The time amount which 5-25 degrees C and cooling take 0-35 degrees C of temperature to cool preferably is 4 - 10 hours preferably for 2 to 15 hours.

[0017] Since it is the complicated constituent with which physical properties, such as the boiling point, approximate with the specified substance, and contain many polar substances other than hydrocarbons, such as a straight chain mold and a side-chain mold, in order to condense squalane by the high grade effectively, to improve the dispersibility of a raw material and an organic solvent and to raise the degree of freedom of a urea or thiourea, as for the raw material dealt with by this invention, it is also desirable to make temperature high and to mix. Even if it carries out in ordinary temperature, inclusion is performed, but if selectivity is bad and tends to condense squalane to a high grade, the amount of a urea or the thiourea used increases, yield falls, and it cannot be said that it is effective. Moreover, although cooling does not necessarily need to be carried out, in temperature, if cooling is ended above 40 degrees C, inclusion will not be performed, but high-grade-izing of the specified substance is difficult. However, if it cools to low temperature not much, the viscosity of a raw material will become high and yield will worsen. This processing is one of the points with important fully taking a cooldown delay. As for rapid cooling, it becomes difficult for the crystal of a urea or thiourea to become fine, and for the selectivity of about [ that the next \*\* exception becomes difficult ] and inclusion to fall, and to obtain the squalane of a high grade.

[0018] Thus, after processing, the organic solvent which a urea or thiourea crystallized and used can be removed by the suitable approach, and the vegetable squalane concentrate made into the purpose of this invention can be obtained. Usually, what is necessary is just to carry out separation removal of the organic solvent from filtrate, after carrying out a processing object a \*\* exception and removing a crystal. In this invention, it is 85 - 98%, and a high grade, and nebula, a deposit of a crystal, and the squalane concentrate that does not lose a fluidity, without solidifying can be obtained also under -40-degree C low temperature. Moreover, the extracted concentrate does not have an odor and are tasteless and colorlessness.

[0019]

[Embodiment of the Invention] Next, this invention is explained according to an example.

The olive oil which pressed oil with example 1 conventional method by reduced pressure of 230-250 degrees C and 266-1064Pa A steam topping, Or the saponification deoxidizing method or precision distillation is applied to the obtained distillate (170-190 degrees C and 5-70Pa) of about 35 % of the weight of squalene concentration, and 50 % of the weight or more of free fatty acid contents which carried out bottom thin film distillation of reduced pressure. Free fatty acid was removed, the deoxidation deodorization distillate (iodine number: 308) made into 65 - 80 % of the weight of FUKUWAREN concentration was hydrogenated under pressurization heating, and the water garnish (iodine number: 0.5, 65 - 80 % of the weight of squalane concentration) was obtained to it. 600g of this water garnish was mixed with 200g isopropyl alcohol, and 200g (the 1st class of reagent) of ureas was added. Often mixing, it heated, the temperature up was carried out to 70 degrees C, and mixing was continued as it was for 1 hour, and it cooled slowly so that it might fall 5 degrees C at a time to 25 degrees C after that in 1 hour. After becoming 25 degrees C and riping for 2 hours, the crystal was carried out the \*\* exception and removed. The obtained filtrate was put and separation removal of the isopropyl alcohol was carried out, and the concentrate which remained was rinsed, it dehydrated, and 540g of vegetable squalane concentrates of the ORIBU origin was obtained. The squalane purity in this concentrate (based on a gas-chromatography measuring method) was 93%, and it did not lose a fluidity, without having also set at -45 degrees C, and having deposited and a nebula crystal solidifying.

Moreover, there was no odor and they were tasteless and colorless.

[0020] Hydrogenation of the distillate (iodine number: 270) which carried out thin film distillation under reduced pressure of 170-190 degrees C and 5-70Pa, and obtained the soybean crude oil which carried out the hexane extract and obtained example 2 soybean after carrying out degumming deoxidation with a conventional method was carried out with the conventional method. It heats to 60 degrees C, adding 100g of ureas and mixing [ mix ethanol 300g with 300g (iodine number: 0.8) of obtained water garnishes 95%, ]. After mixing as it is for 1 hour, it cooled so that it might fall 10 degrees C at a time in 1 hour, and was made 20 degrees C. After riping for 2 hours, it carried out the \*\* exception by the suitable approach. By carrying out separation removal of the solvent, the purity of the vegetable squalane of the soybean origin was 95%, and a fluidity was not lost, either, without having deposited and at least -40 degrees C of nebula and crystals solidifying. Moreover, there was no odor and they were tasteless and colorless.

[0021] Hydrogenation of the deoxidation deodorization distillate (iodine number: 270) which processed example 3 rice bran oil like the example 1, and obtained it was carried out with the conventional method. 600g (iodine number: 0.3) of obtained water garnishes was dissolved in 600ml benzene, and 400g of ureas was added. It heats to 60 degrees C, often mixing. After mixing as it is for 1 hour, it cooled so that it might fall 5 degrees C at a time in 1 hour, and was made 20 degrees C. After riping for 2 hours, the crystal was carried out the \*\* exception. The benzene of the obtained filtrate was distilled off and 420g of vegetable squalane concentrates of the rice bran origin was obtained. The purity of this vegetable squalane was 98%, there is no deposit of nebula, solidification, and a crystal and at least -45 degrees C of fluidities were not lost, either. Moreover, there was no odor and they were tasteless and colorless.

[0022] Example of comparison 1 example 1 was altogether operated in ordinary temperature. Although obtained, purity (based on a gas-chromatography measuring method) is 83%, and produced nebula at -20 degrees C.

[0023] In actuation of example of comparison 2 example 1, cooling was processed at 45 degrees C at a stop and this appearance. The purity of the obtained squalane is 76% and produced nebula at -20 degrees C.

[0024] In actuation of example of comparison 3 example 1, isopropyl alcohol was not added but it processed similarly. The purity of the obtained squalane is 70% and produced nebula at -20 degrees C.

[0025] In actuation of example of comparison 4 example 2, 10g added and water was processed similarly. The purity of the obtained squalane is 68% and was solidified at -10 degrees C.

[0026] 200g (iodine number: 308) of obtained deoxidation deodorization distillates (a steam topping or 170-190 degrees C, and 5-70Pa) which carried out bottom thin film distillation of reduced pressure was mixed with 1000g isopropyl alcohol for the olive oil which pressed oil with example 4 conventional method by reduced pressure of 230-250 degrees C and 266-1064Pa, and 200g (the 1st class of reagent) of ureas was added. After heated, having carried out the temperature up to 70 degrees C, having continued mixing as it was for 1 hour, having cooled slowly so that it might fall 5 degrees C at a time to 15 degrees C after that in 1 hour, and continuing mixing at 15 degrees C for further 2 hours, often mixing, the depositing crystal was carried out the \*\* exception and removed. The obtained filtrate was put, separation removal of the isopropyl alcohol was carried out, rinsing dehydration of the oil which remained was carried out, and 140g of vegetable squalene concentrates was obtained. Hydrogenation of this was carried out with the conventional method, and it considered as the squalane concentrate. The squalane purity in this concentrate was 92%, and it did not lose a fluidity, without having also set at -40 degrees C, and having deposited and nebula and a crystal solidifying. Moreover, there was no odor and they were tasteless and colorless.

[0027] 500g (iodine number: 270) of deoxidation deodorization distillates which processed example 5 rice bran oil like the example 4, and obtained it was dissolved in 1000g benzene, and 500g of ureas was added. After heating to 60 degrees C and continuing mixing as it was for 1 hour, often mixing, it cooled so that it might fall 5 degrees C at a time in 1 hour, and was made 15 degrees C. After continuing mixing at 15 degrees C for further 2 hours, the crystal was carried out the \*\* exception. The benzene of

the obtained filtrate was distilled off and 280g of vegetable squalene concentrates was obtained. Hydrogenation of this was carried out with the conventional method, and it considered as the squalane concentrate. The purity of the squalane in this concentrate was 94%, there is no deposit of nebula, solidification, and a crystal and at least -40 degrees C of fluidities were not lost, either. Moreover, there was also no odor and they were tasteless and colorlessness.

[Effect of the Invention] By the approach of this invention, hydrogenation of the squalene contained in vegetable oil and fat or a deoxidation deodorization distillate can be carried out, it can consider as squalane, and the colorless, odorless squalane of a high grade can be easily obtained from the impurity with which the squalane, the chemical structure, and the physical properties which are intermingled in a distillate are similar. In addition, the approach of this invention is easy equipment which needs neither a proof-pressure container nor a special cooling system, is very simple actuation and can be enforced comparatively efficiently in a short time.

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(54) 【発明の名称】 植物性スクワラン濃縮物の製造方法

(57) 【要約】

【課題】 食用油の製造工程で生成するスクワレン含有留出物等を用いて、高純度のスクワラン濃縮物を得る。

【解決手段】 A) スクワレンを含有する植物性油脂又はその脱酸脱臭留出物を水添した後に、有機溶媒中で、尿素又はチオ尿素処理し、不純物を除去する方法、又は B) スクワレンを含有する植物性油脂又はその脱酸脱臭留出物をそのまま尿素又はチオ尿素処理し、不純物を除去した後に、水添する方法で植物性スクワラン濃縮物を製造する。なお、尿素又はチオ尿素処理は、原料を有機溶媒及び尿素又はチオ尿素と混合して得た水分含有率8重量%以下の混合物を、40～120℃に加熱し、その後0～35℃に冷却するという方法で実施する。



## 【特許請求の範囲】

【請求項1】 スクワレンを含有する植物性油脂又はその脱酸脱臭留出物の水添物を、有機溶媒と尿素又はチオ尿素と混合して得た水分含有率8重量%以下の混合物を、40～120℃に加熱し、その後0～35℃に冷却した後、尿素又はチオ尿素の結晶及び前記有機溶媒を除去して、スクワレン純度が85%以上であり、-40℃でも白濁せず、流動性ある濃縮物を得ることを特徴とする植物性スクワレン濃縮物の製造方法。

【請求項2】 植物性油脂がオリーブ油、トウモロコシ油、大豆油、ペニバナ油、米糠油、小麦胚芽油、パーム油及びゴマ油からなる群より選ばれる少なくとも一種である請求項1の方法。

【請求項3】 有機溶媒がアルコール系溶媒、グリコール系溶媒及び炭化水素系溶媒からなる群から選ばれる請求項1又は2の方法。

【請求項4】 上記水添物のヨウ素価が1以下である請求項1～3いずれか1項の方法。

【請求項5】 スクワレンを含有する植物性油脂又はその脱酸脱臭留出物を、有機溶媒と尿素又はチオ尿素と混合して得た水分含有率8重量%以下の混合物を、40～120℃に加熱し、その後0～35℃に冷却した後、尿素又はチオ尿素の結晶及び前記有機溶媒を除去し、得られた製品を水添し、スクワレン純度が85%以上であり、-40℃でも白濁せず、流動性ある濃縮物を得ることを特徴とする植物性スクワレン濃縮物の製造方法。

【請求項6】 植物性油脂がオリーブ油、トウモロコシ油、大豆油、ペニバナ油、米糠油、小麦胚芽油、パーム油及びゴマ油からなる群より選ばれる少なくとも一種である請求項5の方法。

【請求項7】 有機溶媒がアルコール系溶媒、グリコール系溶媒及び炭化水素系溶媒からなる群から選ばれる請求項5又は6の方法。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】 本発明は、化粧品、医薬品等の分野において有用な植物性スクワレンの濃縮に関する。

## 【0002】

【従来の技術】 化粧品及び医薬品用原料として利用されている炭化水素は石油由来の炭化水素である流動パラフィンに代表される炭化水素と生物由来であるスクワレンに代表される炭化水素とに分類される。スクワレンは無色、無臭、無味の低揮発性の油状液体で、流動パラフィンに比べより軽い油性の感触を持ち、皮膚に対する浸透性、潤滑性に優れ、また非常に伸びが良く、かつ乳化しやすいため、最も優れた化粧品、医薬品の油相原料の一つとされている。

【0003】 従来、使用されてきた天然スクワレンはアイザメに代表される主として深海産鯨を出発原料とする

動物性スクワレンである。この動物性スクワレンはアイザメ等の肝油中から分取されるスクワレンを水添したもので、凝固点が-55℃以下と低温安定性に優れ、安全性も高い。

【0004】 ところが近年になって、実質的に唯一天然スクワレンの原料である深海産鯨の主産地である、フィリピン、インドネシア、インド、スリランカ、アフリカ西海岸、カリブ海では気候の変化、乱獲などで漁獲高が低下し、供給量が需要量に追いつかず逼迫の傾向が続いている。また、最近の動物愛護運動の高まりが更に一層逼迫の傾向に拍車をかけることは充分予測出来ることである。更に、動物由来の天然資源を忌避する傾向も年々強くなっている。

## 【0005】

【発明が解決しようとする課題】 そこで、本発明者らは、天然スクワレンの原料として植物由来のスクワレンに着目した。スクワレンが植物特に果実及び種子中に含まれていることは古くから知られていたが、その含有量は極めて少なく、スクワレンを工業的に抽出、分離、濃縮することは非常に困難であり、工業化は不可能と考えられてきた。例えば比較的多量に含まれていると言われるオリーブ油でも、そのスクワレン含有量は0.2～0.7重量%である。

【0006】 ところで、オリーブ油をはじめ食用油はその精製工程で脱酸脱臭を行うが、この時の留出物としてスクワレンが、遊離脂肪酸やスクワレン以外の様々な不けん化物と一緒に得られる。この留出物は、食用油を製造する時に、必ず生成されるものであるから、この留出物から効果的にスクワレンが抽出、分離、濃縮できれば、安定して植物由来のスクワレンを供給できる。

【0007】 しかし、オリーブ油をはじめ食用油の脱酸脱臭留出物に含まれる不けん化物の組成は、炭化水素類、ステロール類、メチルステロール類、トリテルペン類、トコフェロールなど多岐にわたり、スクワレンと物性が近似している成分も多く含まれている。そのため、スクワレンを高濃度に濃縮することは大変困難であるとされてきた。

## 【0008】

【課題を解決するための手段】 本発明等は、スクワレンを含有する植物性油脂又はその脱酸脱臭留出物の水添物を、有機溶媒中で尿素又はチオ尿素処理するか、又は、前記植物性油脂又はその脱酸脱臭留出物を、有機溶媒中で尿素又はチオ尿素処理し、その後に水添することにより、植物性スクワレンを効率よく濃縮できることを見いだした。

【0009】 本発明に利用できる原料は、オリーブ油、トウモロコシ油、大豆油、ペニバナ油、米ぬか油、小麦胚芽油、パーム油等又はそれらの脱酸脱臭留出物であるが、好ましくはオリーブ油、トウモロコシ油又は米ぬか油であり、更に好ましくはオリーブ油、トウモロコシ油又は

米ぬか油の脱酸脱臭留出物である。これらの原料は必ずしも単一種類でなくともよく、二種類以上を混合してもよい。

【0010】本発明では、前述の如く、A)原料を水添した後に、有機溶媒中で、尿素又はチオ尿素処理し、不純物を除去する方法で、主に植物性スクワラン濃縮物を製造するが、B)原料をそのまま尿素又はチオ尿素処理し、不純物を除去し、スクワレンを濃縮した後に、水添する方法で植物性スクワラン濃縮物を製造することもできる。いずれの方法においても、尿素又はチオ尿素処理は、原料(又は原料の水添物)を有機溶媒と尿素又はチオ尿素とを混合して得た水分含有率8重量%以下(6重量%以下、特に5重量%以下であるのが好ましい)の混合物を、40~120℃に加熱し、その後0~35℃に冷却するという方法で実施されるのがよい。冷却後、尿素又はチオ尿素の結晶及び前記有機溶媒を除去することにより、A)法では、直接、また、B)法では、得られた製品(スクワレン濃縮物)を常法に従って水添することにより、スクワラン純度が85%以上であり、-40℃でも白濁せず、流動性あるスクワラン濃縮物を得ることができる。

【0011】なお、水添はニッケル触媒等を用い、常圧又は加圧下に行う公知の方法を使用できる。本発明では、前述の如く、A)法及びB)法のいずれが適用されてもよいが、A)法で、原料を、尿素又はチオ尿素処理するのに先立ち、水添し、ヨウ素価1以下にしておくことにより、非常に効率よく高純度のスクワランを得ることができる。ただし、ヨウ素価が1を越えたまま尿素又はチオ尿素処理すれば、再度水添を行わなければならない。本発明の目的であるスクワランの収率の低下を招き、また、工程を複雑化するので、有利な方法とは言えない。なお、水添に先立ち脱酸処理をしたり、また、水添と尿素又はチオ尿素処理の間に精留処理をするなど、付加的な処理をしてもよい。

【0012】これに対して、B)法一水添を行わずに尿素又はチオ尿素処理する方法一は、不純物の主たる組成物である直鎖不飽和炭化水素(スクワレンと炭素数が同程度)とスクワレンとの尿素又はチオ尿素による包接分別効果が、スクワレンと炭素数が同程度の直鎖飽和炭化水素とスクワレンとのそれよりも小さいため、かかる不純物(直鎖不飽和炭化水素)の除去に、より多量の尿素又はチオ尿素が必要となり、また同時にスクワレンの収率が低下するので、A)法よりは、多少効率の劣るものとなる。

【0013】本発明において、有機溶媒としては、ハロゲン化炭化水素系、ケトン系、炭化水素系、アルコール系、エステル系等がいずれも使用でき、その混合物が使用されてもよいが、n-アルカン、n-アルケン、直鎖飽和脂肪酸系エステル等の使用は、処理に支障があり、好ましくない。好ましいものは、ケトン系、アルコール

系、炭化水素系溶媒であり、アルコール系溶媒、特にC<sub>1</sub>~C<sub>4</sub>の使用が好ましい。これらの溶媒の使用量は、少量であれば、目的物の収率が低下するのみならず、作業性もよくなく、また多量であれば、溶媒のロスが大きく、また設備や製造コストの増大につながる。一般に、原料の重量に対して0.2~100倍の使用が適当であり、特に0.3~10倍程度の使用が好ましい。

【0014】更に、尿素又はチオ尿素としては、市販のJIS規格に適合している工業用尿素及び工業用チオ尿素が使用できる。尿素及びチオ尿素の使用量は、原料に含まれる不純物の量によって決められるが、少量であれば、不純物の除去が充分に行われず再度処理を繰り返さなくてはならなくなる。多量であれば、不純物だけでなく、目的物たるスクワランも同時に包接され収率の低下を招く。その使用量は、原料重量に対して0.2~20倍、特に0.3~5倍程度であるのが好ましい。

【0015】かかる尿素又はチオ尿素処理は、原料と有機溶媒と尿素又はチオ尿素を同時に又は逐次に、反応機(攪拌機又は振とう機を持ち、加熱及び冷却でき、かつコンデンサーを持つ、ステンレス製又はガラスライニング製の密閉できる容器)に仕込んで実施されればよいが、通常、原料を有機溶媒に溶解ないしは分散させた溶液に、尿素又はチオ尿素を添加するのが好ましい。ただし、仕込みの順序は処理効果に影響しない。

【0016】所定量の原料、有機溶媒及び尿素又はチオ尿素を仕込み、攪拌又は振とうしながら、常温又は40~120℃、好ましくは50~80℃で充分混合させる。充分混合されたことを確認してから、ゆっくりと冷却する。冷却する温度は、0~35℃、好ましくは5~25℃、冷却に要する時間は2~15時間、好ましくは4~10時間である。

【0017】本発明で取り扱う原料は、沸点等の物性が目的物と近似し、直鎖型、側鎖型等の炭化水素類のほか多くの極性物質を含有する複雑な組成物であるので、効果的にスクワランを高純度で濃縮するには、原料と有機溶媒との分散性を良くし、かつ尿素又はチオ尿素の自由度を高めるために、温度を高くして混合することも望ましい。常温で行っても包接は行われるが、選択性が悪く、スクワランを高純度に濃縮しようとすれば、尿素又はチオ尿素の使用量が多くなり、収率が低下し、効果的といえない。また、冷却は必ずしも実施される必要はないが、温度を40℃以上で冷却を終了すれば、包接が行われず、目的物の高純度化は困難である。しかし、あまり低温まで冷却すると原料の粘度が高くなり収率が悪くなる。かかる処理は、冷却時間を充分に取ることが重要な点の一つである。急速な冷却は、尿素又はチオ尿素の結晶が細くなり、次の分別が困難になるばかりか、包接の選択性が低下し、高純度のスクワランを得ることが困難となる。

【0018】このように処理した後、尿素又はチオ尿素

の結晶及び使用した有機溶媒を適当な方法で除去し、本発明の目的とする植物性スクワラン濃縮物を得ることができる。通常、処理物を汙別し、結晶を除去した後、汙液から有機溶媒を分離除去すればよい。本発明では、85～98%と高純度であり、-40℃の低温下でも白濁、結晶の析出、固化することなく、流動性を失わないスクワラン濃縮物を得ることができる。また、採取した濃縮物は臭気がなく、無味、無色である。

#### 【0019】

【発明の実施の形態】次に本発明を実施例に従って説明する。

#### 実施例1

常法により搾油したオリブ油を230～250℃、266～1064Paの減圧で水蒸気トッピング、又は170～190℃、5～70Paの減圧下薄膜蒸留して得たスクワレン濃度約35重量%、遊離脂肪酸含有量50重量%以上の留出物に、ケン化脱酸法又は精密蒸留法を適用して、遊離脂肪酸を除去し、フクワレン濃度65～80重量%とした脱酸脱臭留出物(ヨウ素価:308)に、加圧加熱下で水素添加して、水添物(ヨウ素価:0.5、スクワラン濃度65～80重量%)を得た。この水添物600gを200gのイソプロピルアルコールと混合し、尿素(試薬1級)200gを添加した。よく混合しながら、加熱して、70℃まで昇温し、1時間そのまま混合を続け、その後、25℃まで1時間に5℃づつ下がるようにゆっくり冷却した。25℃になってから2時間熟成した後、結晶を汙別して除去した。得られた汙液を静置してイソプロピルアルコールを分離除去し、残った濃縮物を水洗、脱水してオリブ由来の植物性スクワラン濃縮物540gを得た。この濃縮物中のスクワラン純度(ガスクロマトグラフィー測定法による)は93%であり、-45℃においても白濁結晶の析出、固化することなく、流動性を失わなかった。また、臭気はなく、無味、無色であった。

#### 【0020】実施例2

大豆をヘキサン抽出して得た大豆原油を、常法により脱ガム脱酸した後、170～190℃、5～70Paの減圧下、薄膜蒸留して得た留出物(ヨウ素価:270)を常法により水添した。得られた水添物(ヨウ素価:0.8)300gと95%エタノール300gを混合し、尿素100gを添加して混合しながら60℃まで加熱する。1時間そのまま混合した後、1時間に10℃づつ下がるように冷却し、20℃にした。2時間熟成した後、適当な方法で汙別した。溶媒を分離除去して大豆由来の植物性スクワランの純度は95%であり、-40℃でも白濁、結晶の析出、固化することなく、流動性も失わなかった。また、臭気はなく、無味、無色であった。

#### 【0021】実施例3

米ぬか油を実施例1と同様に処理して得た脱酸脱臭留出物(ヨウ素価:270)を常法により水添した。得られ

た水添物(ヨウ素価:0.3)600gを600mlのベンゼンに溶解し、尿素400gを添加した。よく混合しながら60℃まで加熱する。1時間そのまま混合した後、1時間に5℃づつ下がるように冷却し、20℃にした。2時間熟成した後、結晶を汙別した。得られた汙液のベンゼンを留去して米ぬか由来の植物性スクワラン濃縮物420gを得た。この植物性スクワランの純度は98%であり、-45℃でも白濁、固化、結晶の析出はなく、流動性も失われなかった。また、臭気はなく、無味、無色であった。

#### 【0022】比較例1

実施例1の操作を全て常温で行った。得られたものの純度(ガスクロマトグラフィー測定法による)は83%であり、-20℃で白濁を生じた。

#### 【0023】比較例2

実施例1の操作において、冷却を45℃に止め、同様に処理した。得られたスクワランの純度は76%であり、-20℃で白濁を生じた。

#### 【0024】比較例3

20 実施例1の操作において、イソプロピルアルコールを添加せず、同様に処理した。得られたスクワランの純度は70%であり、-20℃で白濁を生じた。

#### 【0025】比較例4

実施例2の操作において、水を10g添加して、同様に処理した。得られたスクワランの純度は68%であり、-10℃で固化した。

#### 【0026】実施例4

常法により搾油したオリブ油を230～250℃、266～1064Paの減圧で水蒸気トッピング、又は170～190℃、5～70Paの減圧下薄膜蒸留して得た脱酸脱臭留出物(ヨウ素価:308)200gを、1000gのイソプロピルアルコールと混合し、尿素(試薬1級)200gを添加した。よく混合しながら、加熱して、70℃まで昇温し、1時間そのまま混合を続け、その後、15℃まで1時間に5℃づつ下がるようにゆっくり冷却し、15℃で更に2時間混合を続けた後、析出した結晶を汙別して除去した。得られた汙液を静置してイソプロピルアルコールを分離除去し、残った油分を水洗脱水して植物性スクワレン濃縮物140gを得た。これを常法により水添し、スクワラン濃縮物とした。この濃縮物中のスクワラン純度は92%であり、-40℃においても白濁、結晶の析出、固化することなく、流動性を失わなかった。また、臭気はなく、無味、無色であった。

#### 【0027】実施例5

米ぬか油を実施例4と同様に処理して得た脱酸脱臭留出物(ヨウ素価:270)500gを1000gのベンゼンに溶解し、尿素500gを添加した。よく混合しながら60℃まで加熱し、そのまま1時間混合を続けた後、1時間に5℃づつ下がるように冷却し、15℃にした。

15℃で更に2時間混合を続けた後、結晶を汙別した。得られた汙液のベンゼンを留去して、植物性スクワレン濃縮物280gを得た。これを常法により水添し、スクワラン濃縮物とした。この濃縮物中のスクワランの純度は94%であり、-40℃でも白濁、固化、結晶の析出はなく、流動性も失われなかった。また、臭気もなく、無味、無色であった。

【発明の効果】本発明の方法では、植物油脂又は脱酸脱

臭留出物に含まれるスクワレンを水添してスクワランとし、留出物中に混在するスクワランと化学構造及び物性が類似する不純物から、簡単に、高純度の無色無臭のスクワランを得ることができる。なお、本発明の方法は、耐圧容器や特殊な冷却装置を必要としない簡単な装置で、非常に簡便な操作で、比較的短時間に効率よく実施できる。

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